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Accurate structures from combined gas electron diffraction and liquid crystal NMR data; the importance of anisotropy of indirect couplings for 1,4-difluorobenzene†

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Gas-phase electron-diffraction scattering data and dipolar couplings from NMR experiments in four different liquid crystal solvents have been combined to give a high-accuracy molecular structure of 1,4-difluorobenzene. The anisotropic components of the CF and FF indirect couplings have been deduced directly from the experimental data. The resultant structure has standard deviations of around 0.2 pm for interatomic distances and less than 0.2° for inter-bond angles.

Introduction

Simultaneous analysis of structural data obtained by several techniques often yields a complete and accurate structure, whereas data from one technique alone would give an incomplete and/or less accurate set of parameters. Although a method that utilises both experimental and theoretical data exists (SARACEN^{1–3}), purely experimental analyses are preferable for suitable molecules. Gas-phase electron diffraction (GED) data and rotation constants are routinely combined, and we have also been able to use dipolar couplings, obtained from NMR spectra of solutions in liquid-crystal solvents (LCNMR). The latter combination has been particularly successful for aromatic rings, for which the absence of low-frequency vibrational modes has been a significant beneficial factor.^{4–6}

A systematic study of chlorinated benzenes^{6–13} was undertaken primarily to assess the validity of combining gas-phase and solution-phase data, and it has been demonstrated that the accuracy of these combined analyses matches their impressive precision.¹⁴ Interactions between solvents and solutes do not distort the structures significantly. The investigation of this series of chlorobenzenes also showed the effects of multiple substitution. Replacement of hydrogen by chlorine results in several changes to the ring structure, of which the most important are shortening of the C–C bonds adjacent to the substituent, widening of the ring angle at the substituent site, and a smaller narrowing of the two neighbouring ring angles. On multiple substitution the effects are largely additive, but there are also further distortions, mainly attributable to steric interactions between adjacent substituents.

Fluorine causes greater distortions than chlorine, because the magnitudes of substitution effects depend to a large extent on the electronegativity of the substituent,¹⁵ but steric effects arising from fluorine substituents on adjacent carbon atoms are not significant.¹⁶ The family of fluorobenzenes should therefore be well suited to a systematic investigation of multiple substitution effects. However, there are some experimental difficulties. In electron-diffraction studies, the similarity of C–F and C–C distances (and consequently of non-bonded C...F and C...C distances) leads to correlation between geometrical parameters. In rotational spectroscopy, the existence of only one stable isotope of fluorine reduces the number of independent rotation constants that can be measured. The spin-1/2 ¹⁹F nucleus increases the amount of information that can be obtained by liquid-crystal NMR spectroscopy, but care must be taken to ensure that anisotropy of ¹³C¹⁹F and ¹⁹F¹⁹F indirect couplings does not introduce errors.

We have now studied the three isomers of difluorobenzene. Combined analyses of electron diffraction data, rotation constants and dipolar coupling constants for 1,2- and 1,3-difluorobenzene will be published elsewhere.¹⁷ In the case of 1,4-difluorobenzene, the absence of a dipole moment precludes the measurement of rotation constants by microwave spectroscopy. In this paper we present the results of a combined analysis of electron diffraction and liquid-crystal NMR data. Sufficient experimental data are available to allow us to refine the anisotropy of all four indirect ¹³C¹⁹F coupling constants and that of the ¹⁹F¹⁹F coupling constant.

Experimental

A sample of 1,4-difluorobenzene (purity 99%) was purchased from Aldrich and used without further purification. GED data were recorded on Kodak Electron Image plates using the Edinburgh apparatus¹⁸ operating at 44.5 kV, and obtained in digital form using a Joyce Loebl MDM6 microdensitometer at the EPSRC Daresbury Laboratory.¹⁹ During experiments the sample and nozzle were maintained at 293 K. Data for benzene were also recorded, to provide calibration of the

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† Electronic supplementary information (ESI) available: List of LCNMR direct coupling constants for 1,4-difluorobenzene; experimental details from the combined electron-diffraction and LCNMR refinement; interatomic distances, amplitudes of vibration and the least-squares correlation matrix from the refinement; Cartesian coordinates for the final refined structure; the molecular-intensity scattering curves (Tables S1–S5, Fig. S1). See DOI: 10.1039/b708842f

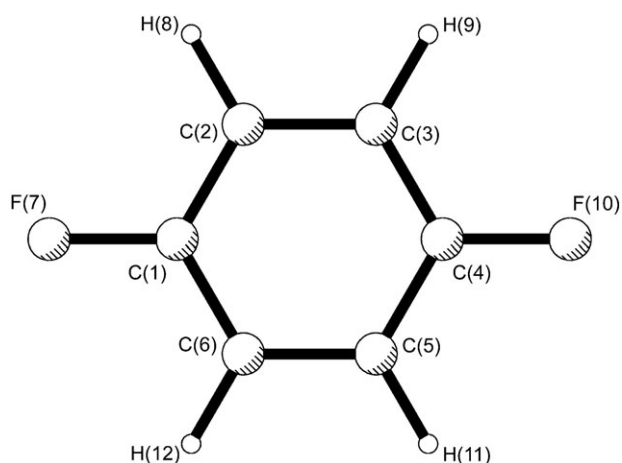


Fig. 1 The molecular structure of 1,4-difluorobenzene, showing the atom numbering.

electron wavelength and camera distances. Other experimental data are listed in Table S1.† Data reduction and least-squares refinements were performed using *ed@ed* version 2.3,²⁰ and the scattering factors of Ross *et al.*²¹

Dipolar coupling constants, measured in the liquid-crystal-line solvents ZLI 1167, ZLI 1132, ZLI 1695 and a mixture of ZLI 1167 (58.9% by weight) and Merck Phase IV, were taken from the literature.²² They are listed in Table S2 alongside their values after being corrected for the effects of vibrations, as described below. The atom numbering is given in Fig. 1.

The weights given to the experimental data during the least-squares refinement are important. For the GED data, an off-diagonal weight matrix is used with elements defined as

$$w_{ii} = (s_i - s_{\min}) / (sw_1 - s_{\min}) \quad s_{\min} \leq s_i \leq sw_1$$

$$w_{ii} = 1 \quad sw_1 \leq s_i \leq sw_2$$

$$w_{ii} = (s_{\max} - s_i) / (s_{\max} - sw_2) \quad sw_2 \leq s_i \leq s_{\max}$$

$$w_{ij} = 0 \quad i \neq j \pm 1$$

$$w_{ij} = -0.5(w_{ii} + w_{jj})q_k \quad i = j \pm 1$$

where sw_1 and sw_2 are weighting points for the distance k and are chosen by inspection, and q is the correlation parameter. For the LCNMR data, the weight matrix is extended with diagonal terms only. These diagonal weighting terms are inversely proportional to the squared uncertainties of the observations and are scaled to the standard deviation of the fit of the ED data points.

Results and discussion

Molecular model

For all structural analyses it was assumed that 1,4-difluorobenzene has D_{2h} symmetry. Its geometry is defined by two different ring C–C distances, the C–F and C–H bond lengths, one ring angle and an angle locating the hydrogen atoms. In practice the chosen parameters were the average (not weighted) of the distances C(1)–C(2) and C(2)–C(3) and the

difference between them, the C–F and C–H distances, the angle C(6)–C(1)–C(2), and an angle defining the deviation of the C–H bonds from the bisectors of the adjacent C–C–C angles, a positive deviation reflecting displacement of the hydrogen atoms towards the neighbouring fluorine atom. See Fig. 1 for atom numbering.

Force field

Before refinement of the structure could begin, it was necessary to derive a force field, from which vibrational amplitudes could be calculated, as well as other vibrational terms needed to relate the experimental data to a common structural base (r_{h0}). In an earlier NMR study of 1,4-difluorobenzene²² the force field for 1,4-dichlorobenzene was modified (details of the modification are not given) and used to calculate vibrational corrections. The errors in the vibrationally corrected dipolar couplings, used to weight the observations in the structural analysis, were assumed to be the same as those for the uncorrected couplings, so the force field and correction terms derived from it were tacitly assumed to be absolutely correct. We have preferred to generate a force field using the molecular mechanics program MM3,²³ as this is based on experimental data for a very large number of molecules. A force field derived by *ab initio* calculations could be used, but in this particular case we are basing the entire analysis on experimental data. The program ASYM²⁴ was then used to calculate amplitudes of vibration, used as starting values for the GED refinement, and the parallel and perpendicular vibrational corrections needed in the analysis of electron-diffraction data. It was not possible to refine an r_{h1} structure because the vibrational correction terms allowing for curvilinear motions cannot at present be calculated for dipolar coupling constants. However, for a reasonably rigid planar molecule this is not a serious limitation. A small modification to ASYM (now included as standard) was necessary so that the covariance matrices, used to correct the dipolar couplings (from D_0 to D_α), could be calculated. These matrices depend on the expectation values of the terms $\Delta x \Delta y$, $\Delta x \Delta z$ and $\Delta y \Delta z$, where Δx , Δy and Δz are the components of the instantaneous excursion of the internuclear vector from the equilibrium position.

The corrections to dipolar coupling constants obtained in this way are not identical to those used in the earlier work,²² and some discrepancies are substantial. As an extreme example, for $D_{2,8}$ in ZLI 1132 the two values of the correction are 146.99 and 137.27 Hz, although the uncertainty in the observed coupling is only 0.16 Hz. It is not possible to draw any firm conclusions as to which set of corrections is better, but it is clear that any set must be treated with appropriate caution. A survey of the results of this and some previous studies of aromatic compounds^{4,6,25} indicates that the uncertainties are roughly proportional to the magnitudes of the correction terms, and that 10% of the magnitude, with a lower limit of 0.1 Hz, is a reasonable and safe figure to use in assigning uncertainties. With a force field calculated *ab initio* at a very high level, one could take a less conservative position, but we would not at present go below 2 or 3% of the *ab initio* magnitude. An immediate and important consequence of this

is that the weights given to the dipolar couplings in our analyses are lower, and in some cases much lower, than those used for the corresponding data in earlier work. (Compare the uncertainty column of Table S2† with the errors given in Tables 2 and 3 in ref. 22.) We believe it is possible that some of the apparent variations in the structures of molecules in different liquid-crystalline solvents result from exact fitting of over-precise data. This can be a particularly severe problem in cases where the number of independent observations is not in large excess over the number of refined structural and orientation parameters. Moreover, observed dipolar coupling constants may be highly correlated, and the number of *independent* observations may be less than the total numbers of observations. Combining gas electron diffraction and dipolar coupling constant data helps to reduce these correlations, and gives a more robust experimental data set.

Structure refinement

The R factor gives an indication of the goodness of fit, where R_G includes the off-diagonal points of the least-squares weight matrix (thus taking into account the effects of correlation of data points) and R_D does not. Using electron-diffraction data alone, the R_G quickly dropped to 0.062, with only the four parameters defining heavy-atom positions refining. Including amplitudes of vibration for heavy atom–heavy atom distances gave $R_G = 0.052$ and changing the structure type from r_a to r_{h0} improved this to 0.049. At this point an attempt was made to refine the remaining two structural parameters, but although $rC-H$ refined reasonably to 108.3(5) pm, the C–H deviation angle could not be refined.

The NMR data obtained for a solution in the liquid-crystal solvent ZLI 1167 were then introduced and the C–H deviation angle now refined to a chemically sensible value. It was noticeable that the differences between the corrected coupling constants and those calculated from the refining geometry using the *ed@ed* program were close to the assigned uncertainties for all coupling constants other than those involving fluorine-to-carbon and fluorine-to-fluorine coupling. As was noted in the original NMR study,²² this apparent discrepancy could be attributed to anisotropic components of one or more of the indirect coupling constants involving these atoms. The model used for refinement was then amended to include factors that allow for the anisotropy of these CF and FF indirect (J) couplings. It was assumed that each observed coupling constant was the sum of the direct, dipolar coupling, D_{ij} , and a contribution from the anisotropy of the indirect coupling, J_{ij}^{aniso} , given by $J_{ij}^{\text{aniso}} S_{ij}$, where S_{ij} is the orientation parameter for the ij vector. For the couplings for the atom pairs 1–7, 1–10 and 7–10, S_{ij} is simply S_{zz} . For the other two CF atom pairs S_{ij} was calculated from S_{zz} and S_{yy} . The five terms representing anisotropy of the indirect coupling were then included in the refinement. With five additional refining parameters the fit of calculated and measured coupling constants was, of course, much better, but this procedure did not provide any additional structural information. However, when data for the other solvents were included later (see below), valuable information was obtained.

Table 1 Refined parameters (r_{h0}) from the combined GED and LCNMR analysis for 1,4-difluorobenzene and the equivalent MP2/6-311 + + G** (r_e) geometric parameters.^a

Geometric parameters		r_{h0}	r_e
<i>Independent</i>			
p_1	$[rC(1)-C(2) + rC(2)-C(3)]/2$	139.06(10)	139.56
p_2	$[rC(1)-C(2)] - [rC(2)-C(3)]$	−0.59(24)	−0.71
p_3	$rC-F$	134.32(24)	135.09
p_4	$rC-H$	107.94(18)	108.50
p_5	$\angle C(6)-C(1)-C(2)$	122.23(15)	122.3
p_6	$\angle C-H$ deviation ^b	0.80(7)	1.5
<i>Dependent</i>			
d_1	$rC(1)-C(2)$	138.77(11)	139.20
d_2	$rC(2)-C(3)$	139.36(19)	139.91
d_3	$\angle C(1)-C(2)-C(3)$	118.88(7)	118.9
d_4	$\angle C(2)-C(3)-H(9)$	121.36(5)	121.4
<i>Orientation parameters^c</i>			
p_7	S_{yy} ZLI 1167 $^1H/^{19}F$	−0.02895(8)	
p_8	S_{zz} ZLI 1167 $^1H/^{19}F$	−0.04905(8)	
p_9	S_{yy} ZLI 1132 1H	0.06147(16)	
p_{10}	S_{zz} ZLI 1132 1H	0.11472(18)	
p_{11}	S_{yy} ZLI 1695 1H	−0.03823(10)	
p_{12}	S_{zz} ZLI 1695 1H	−0.06049(11)	
p_{13}	S_{yy} ZLI 1167/phase IV $^1H/^{19}F$	0.03800(12)	
p_{14}	S_{zz} ZLI 1167/phase IV $^1H/^{19}F$	0.15987(23)	
p_{15}	S_{yy} ZLI 1132 ^{19}F	0.05418(17)	
p_{16}	S_{zz} ZLI 1132 ^{19}F	0.10286(16)	
p_{17}	S_{yy} ZLI 1695 ^{19}F	−0.03431(10)	
p_{18}	S_{zz} ZLI 1695 ^{19}F	−0.05513(10)	
<i>Anisotropic indirect couplings^b</i>			
p_{19}	$C(1)F(7)$	187.9(578)	
p_{20}	$F(7)F(10)$	−20.6(8)	
p_{21}	$C(1)F(10)$	−8.4(14)	
p_{22}	$C(2)F(10)$	17.7(13)	
p_{23}	$C(2)F(7)$	−12.1(31)	

^a Distances (r) are in pm and angles (\angle) are in degrees. Values in parentheses are the uncertainties on the last digits. ^b For definition see text. ^c For descriptions of solvents see text.

The structure obtained using the ZLI 1167 data was consistent with the NMR data obtained with the solvents ZLI 1132, ZLI 1695 and the ZLI 1167/Merck Phase IV mixture. These data were then also introduced into the refinement as before, including the same anisotropy terms for CF and FF coupling constants as for the first solvent. (The contributions to the observed coupling were different, because the orientation parameters were different.) After refinement of the structure the consistency of uncertainties of dipolar coupling constants and the final differences between experimental and calculated values was excellent. There was only one significant discrepancy, for $D_{1,10}$ in the ZLI 1167/Merck Phase IV mixed solvent (see Table S2),† out of 76 experimental coupling constants.

In this way all of the available experimental data, from NMR and GED experiments, contributed to the final structure. Table 1 shows the final values of geometric parameters, orientation parameters and anisotropic indirect coupling constants.

The goodness of fit to the electron-diffraction data can be assessed visually from the radial-distribution curve in Fig. 2, which was produced by Fourier transform of the molecular-scattering intensity curves shown in Fig. S1. The success of the refinement is also demonstrated by the low R factor: $R_G = 0.047$ ($R_D = 0.032$). A list of all interatomic distances and

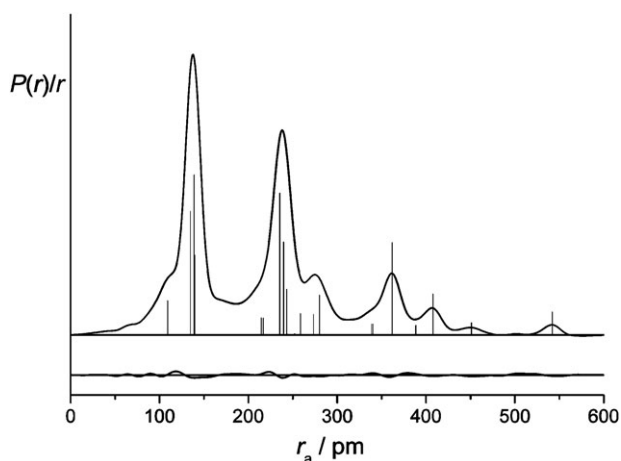


Fig. 2 Experimental GED radial-distribution curve and theoretical-minus-experimental difference curve for the refinement of 1,4-difluorobenzene. Before Fourier inversion the data were multiplied by $\exp(-0.00002s^2)/(Z_C f_C)(Z_F f_F)$. Each stick represents an individual r_a distance.

their corresponding calculated and refined amplitudes of vibration and perpendicular correction terms is given in Table S3, and Table S4 contains the least-squares correlation matrix for the refinement. Coordinates for the final refined structure are given in Table S5.†

The structure of 1,4-difluorobenzene was previously determined by electron diffraction data alone.²⁶ In that study the following parameters were determined: $\angle \text{C-C(F)-C} = 123.5(10)^\circ$; $r_{\text{g}}\text{C-F} = 135.4(4)$ pm; $r_{\text{g}}\text{C-C}_{\text{mean}} = 139.2(3)$ pm (with a difference of 1.2 pm assumed). Using the method pioneered by Domenicano²⁷ the internal ring angles in substituted benzenes can be predicted from an empirically-derived additive model. The distortions associated with having a single fluorine substituent on a benzene ring are $\Delta\alpha_{\text{F}} = 3.4^\circ$, $\Delta\beta_{\text{F}} = -2.0^\circ$, $\Delta\gamma_{\text{F}} = 0.3^\circ$ and $\Delta\delta_{\text{F}} = 0.0^\circ$, where α is the internal ring angle at the substitution site and β , γ and δ are *ortho*, *meta* and *para* to the substituent, respectively. Using these empirical parameters the predicted $\angle \text{C-C(F)-C}$ angle 123.4° is larger than we observe. This is probably because the additive model is less valuable when there are substantial electrostatic interactions. In this case repulsion of the two fluorine atoms might be expected to narrow the ring angles at the substituents.

The geometry of 1,4-difluorobenzene was then calculated using Gaussian 03²⁸ at the MP2/6-311++G** level for comparison with the experimental structure. The values of the calculated parameters are also shown in Table 1. It is pleasing to see that the difference between the two C-C bond lengths is calculated to within one ESD of the experimental value. The accuracy of the internal ring angles is also very impressive.

Conclusion

Here, for the first time, the anisotropies of indirect coupling constants have been determined directly from combined electron-diffraction and liquid-crystal NMR data. Combining data from the gas phase with those measured in solution is only feasible if the solvent does not induce significant distor-

tions of the solute molecules. Our studies of chlorobenzenes¹⁴ indicate that it is reasonable to assume that this is the case, so long as one does not give too much weight to the dipolar coupling constants. Allowance for the uncertainties in the vibrational corrections fortuitously ensures that overdependence on the NMR data is avoided. The complementary nature of the NMR and diffraction data, by which one gives primarily information about ratios of distances, whereas the other gives averages of related distances most accurately, makes the combined method particularly powerful. Using data from a range of solvents allows the anisotropy of indirect coupling constants to be determined. Their magnitudes indicate that direct coupling constants for ^{13}C - ^{19}F and ^{19}F - ^{19}F nuclear pairs should not be used in structure determinations without allowance for anisotropy of indirect coupling.

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